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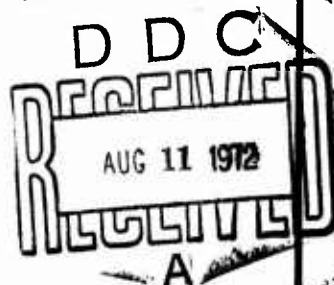
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**RESEARCH AND DEVELOPMENT  
OF  
FLOW-CAST MAGNESIUM FLARES**

**THE DOW CHEMICAL COMPANY**

**TECHNICAL REPORT AFATL-TR-71-120**

**SEPTEMBER 1971**



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**AIR FORCE ARMAMENT LABORATORY**

**AIR FORCE SYSTEMS COMMAND • UNITED STATES AIR FORCE**

**EGLIN AIR FORCE BASE, FLORIDA**

**Research And Development  
Of  
Flow-Cast Magnesium Flares**

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Donald Girardin**

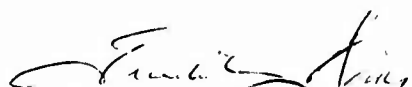
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## FOREWORD

This report covers work performed during the period 3 November 1969 to 3 November 1970 by The Dow Chemical Company, Midland, Michigan, under Contract F08635-70-C-0028, "Research and Development of Flow-Cast Magnesium Flares." The work was sponsored by the Air Force Armament Laboratory, Eglin Air Force Base, Florida, with Capt. Robert H. Dowrie (DLIP) as program monitor.

Management direction at The Dow Chemical Company was under Dr. E. T. Niles, and technical supervision under Dr. G. A. Lane. Major contributions were made by Mr. Erwin M. Jankowiak and Mr. Donald Girardin.

This technical report has been reviewed and is approved.



FRANKLIN C. DAVIES, Colonel, USAF  
Chief, Flame, Incendiary, and Explosives Division

## ABSTRACT

Research and development studies have been conducted on flow-castable magnesium - sodium nitrate flares. The epoxy resins XFS-4008L (glycerin diglycidyl ether) and diglycidyl carbonate were evaluated. The curing agents XF-4012 (partial nitrate salt of amine-terminated polypropylene glycol), maleic anhydride (MA), maleic anhydride - ethylene carbonate (EC), maleic half esters, glycol, benzyldimethylamine and D.E.H.<sup>®</sup>24 (triethylenetetramine) were investigated. TEGDN (triethyleneglycol dinitrate), DEGDN (diethyleneglycol dinitrate), and BDNPA/F [1-1-solution of bis(2,2-dinitropropyl)-acetal and bis(2,2-dinitropropyl)formal] were tested as plasticizers. The most favorable results were obtained with XFS-4008L resin; XF-4012, MA, EC-MA, or D.E.H.<sup>®</sup>24 curing agent; and TEGDN or DEGDN plasticizer. Flare compositions containing these binders can be mixed, poured, and cured; display low spark or impact sensitivity; and are adequately stable in storage at 70°C for 4 to 12 weeks. A "best efforts" composition, containing 22 percent of XFS-4008L - EC-MA - DEGDN binder, yielded an efficiency of 70,000 cd-sec/g (candle-seconds per gram) at 0.056 in/sec (inch per second) burning rate in a 1.25-inch-diameter tape-wrapped flare.

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<sup>a</sup>D.E.H., a trademark of The Dow Chemical Company for epoxy curing agent.

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## GLOSSARY

ADGC - allyl diglycol carbonate.  
BDMA - benzyldimethyl amine.  
BDNPA/F - 1:1 solution of bis(2,2-dinitropropyl)acetal and bis(2,2-dinitropropyl) formal.  
DGC - diglycidyl carbonate.  
DEGDN - diethyleneglycol dinitrate  
D.E.H.<sup>®</sup> 24 - triethylenetetramine.  
D.E.R.<sup>®a</sup> 732 - diglycidyl ether of polypropylene glycol.  
D.E.R.<sup>®</sup> 736 - diglycidyl ether of polypropylene glycol.  
DNA - dinitroaniline.  
DNP - dinitrophenol.  
DNSA - dinitrosalicylic acid.  
EC - ethylene carbonate.  
EC-MA - 1:1 solution of ethylene carbonate and maleic anhydride.  
Half ester D - mixture of 70 percent of the reaction product of two moles of maleic anhydride with one mole of tris polypropylene glycol ether of glycerine and 30 percent of the reaction product of one mole of maleic anhydride with one mole of ethylene glycol mono methyl ether.  
HEA - hydroxyethyl acrylate.  
HEA-MA - reaction product of hydroxyethylacrylate with maleic anhydride.  
MA - maleic anhydride.  
NTA - nitrilotriacetic acid.  
PGNC - plastisol grade nitrocellulose.  
PMA - pyromellitic anhydride.  
PMDA - pyromellitic dianhydride.  
TEA - triethanolamine.  
TEGDN - triethyleneglycol dinitrate.  
XF-4012 - partial nitrate salt of amine - terminated polypropylene glycol.  
XF-4013L - sulfur - containing epoxy resin.  
XFS-4008L - glycerine diglycidyl ether.

<sup>a</sup>D.E.R. , a trademark of The Dow Chemical Company for epoxy resin.

## SOURCES OF MATERIALS

ADGC - PPG Industries  
Acetate tape - Permacel Corporation  
BDMA - Maumee Chemical Company  
Cab-o-sil M-S - Johns Manville Company  
Calcium nitrate - Allied Chemical Company  
Crystal Bay tape - 3M Company  
DEGDN - Commercial Solvents Corporation  
D.E.H.® 24 - The Dow Chemical Company  
D.E.R.® 732 - The Dow Chemical Company  
D.E.R.® 736 - The Dow Chemical Company  
DGC - The Dow Chemical Company  
Diethyloxalate - Eastman Kodak Company  
DL 308 intumescent paint - The Dow Chemical Company  
DNA - J. T. Baker Chemical Company  
DNP - J. T. Baker Chemical Company  
DNSA - Eastman Kodak Company  
EC - Jefferson Chemical Company  
Ethocel tape - The Dow Chemical Company  
Ethylene glycol - The Dow Chemical Company  
Halfester D - The Dow Chemical Company  
HEA - The Dow Chemical Company  
HEA - MA - The Dow Chemical Company  
Hetron polyester - Hooker Chemical Company  
MA - Matheson, Coleman and Bell Company  
Magnesium, atomized - Valley Metallurgical Products Company  
Magnesium oxide - Allied Chemical Company  
Mystic tape - The Borden Company  
NG - E. I. Dupont de Nemours and Company  
NTA - Eastman Kodak Company  
PGNC - E. I. Dupont de Nemours and Company  
PMDA - Princeton Chemical Research, Inc.  
Potassium chlorate - American Potash and Chemical Company  
PVC tape - 3M Company  
Scotch tape - 3M Company  
Sodium nitrate - Davies Nitrate Company  
Sprayon paint - Sprayon Products, Inc.  
TEA - The Dow Chemical Company  
TEGDN - Propellex  
Tris nitro - Commercial Solvents Corporation  
XF-4012 - The Dow Chemical Company  
XF-4013L - The Dow Chemical Company  
XFS-4008L - The Dow Chemical Company

## SECTION I

### INTRODUCTION

The objective of this effort was to develop a pourable, castable magnesium - sodium nitrate flare composition with cured properties required for a military illumination flare. Specifically, the cured flare must maintain a physical and chemical stability over a range of environmental conditions and generate a high level of light output. The composition must be readily and safely manufactured.

Because conventional pressed flare compositions use a minimum of binder (3 to 6 percent) and require high compaction pressure (7000 to 10,000 psi) for physical integrity, this "dry" method of manufacture lacks versatility in adapting to changes in flare design. Additionally, production personnel are often exposed to large quantities of these highly energetic pyrotechnic formulations during operations in which accidental ignitions can occur. In order to minimize or eliminate such production deficiencies, the development of flow-cast flare compositions has been pursued.

It is known that pressed flares generate high levels of radiant output, and dilution of such formulations with additional binder ingredients must necessarily affect light output. However, development work has shown that high radiance can be achieved if a polymeric binder of suitable structure and oxygen content is employed.

This program has emphasized the development of binders specifically tailored for magnesium - sodium nitrate illuminating flares.

In previous work at The Dow Chemical Company, truly castable illuminating flare compositions were developed with as little as 12 percent binder. However, luminous efficiency was only 65 percent of that obtained from pressed flares containing 6 percent of the same binder. Subsequent studies have shown that an efficiency of 40,000 cd-sec/g can be achieved with 18 percent of an oxygen-rich epoxy binder. However, room temperature castability is not good.

More recently under Picatinny Arsenal Contract DAAA21-68-C-0849, both room temperature castability and high efficiency (50,000 cd-sec/g) were attained at the 24 percent binder level by using a high energy nitro-plasticizer. In order to reach these efficiencies not only a nitro-plasticizer but an oxygen-rich epoxy binder system and fine particle size magnesium had to be employed. This work indicated the feasibility of a truly castable, high efficiency flare composition.

The best flow-cast flare composition available at the onset of the present program utilized XFS-4008L epoxy resin cured with XF-4012 curing agent and plasticized with 40 to 50 percent TEGDN. With this system as a point of departure, compositions based on this binder were studied, along with new improved binder systems. The best systems were selected and optimized, and a "best efforts" composition was selected. In the course of the program, attention has been directed at mix properties, rheology, handling safety, curing behavior, cured properties, storage stability, and flare performance.

## SECTION II

### DEVELOPMENT OF EXPERIMENTAL FLARE FORMULATIONS

Fundamental to a practical, high performance flow-cast flare composition is the binder system. Available technology, such as proper sizing of solid particles, use of high-shear mixing, and adjustment of metal-fuel content and binder stoichiometry, is important to accomplishing the task. However, the critical job is to develop a binder system which not only imparts castability to the flare composition but enhances flare performance.

A flow-cast flare composition, based on an improved flare binder, must have sufficient fluidity at the end of the mixing cycle that it can be poured into molds. After casting, the formulation must gel in a reasonable length of time to prevent settling of the solids and cure fast enough to permit practical time cycles in processing. The cured binder must also impart the necessary physical properties to the flare, with maximum light emission and a good combustion rate.

Specifically, the binder must endow a successful flare formulation with the following properties:

- a. Mix viscosity less than 500,000 cps at 25°C.
- b. Pot life of more than 2 to 4 hours.
- c. Low peak exotherm.
- d. High density.
- e. Stability in surveillance at 70°C. for more than 4 weeks.
- f. Insensitive to impact and spark.

The performance of the composition should be such that in a large (3 to 5-inch diameter) flare the luminous efficiency would be in excess of 60,000 cd-sec/g and the burning rate less than 0.09 in./sec.

Essentially, binders consist of a resin or monomer, a curing agent or catalyst, and a functional additive such as a plasticizer for improving castability, processing life, or light output. Because most binders contribute little to light output of a flare composition, it is important to hold binder content to a minimum.

#### A. RESINS

In previous experience at Dow with flow-cast illuminating flare compositions and other pyrotechnic applications, epoxy resins have shown outstanding properties. They have favorable viscosity, wettability, thermal stability, and moisture resistance. They are extremely versatile in curing mechanism

and processing life. Flare compositions based on epoxy binders have displayed high luminous efficiencies and a wide range of burning rates. Because of these advantages, they were selected as the primary polymeric binder type for this development study.

The binder should be high in oxygen content to lower the oxygen demand of the overall flare composition and improve the combustion of the metal-fuel by the oxidizer. Thus, it is imperative that the epoxy resin have the highest possible oxygen content. Of the epoxies available, XFS-4008L (an epoxidized glycerine) and DGC (diglycidyl carbonate) appeared most promising. Both are low in viscosity, with DGC outstanding in this respect, and both have a high oxygen content (39 percent for XFS-4008L and 45 percent for DGC).

Two commercially available epoxy resins, D.E.R.<sup>®</sup> 732 and D.E.R.<sup>®</sup> 736 (diglycidyl ethers of polypropylene glycol), are very low in viscosity. However, because the oxygen content is considerably lower, approximately 27 percent, they were studied on a more limited basis.

Also investigated briefly was the free radical polymerization of experimental, very low viscosity, high oxygen (40 percent) vinyl esters based on HEA-MA (hydroxyethylacrylate - maleic anhydride) and ADGC (allyl diglycol carbonate).

Ethylene glycol (52 percent oxygen) and tris(hydroxymethyl)-nitromethane (53 percent oxygen) were also studied as co-reactants with epoxy resins.

## B PLASTICIZERS

Nitrate esters have proven particularly useful for improving combustion, luminous efficiency, and castability. TEGDN (triethylene glycol dinitrate) is high in oxygen content (52 percent), energetic, and causes dramatic improvement in flare efficiency.

Numerous nitro-plasticizers exist, but many are hazardous to handle and capable of detonation. TEGDN, however, is relatively safe and is a basic plasticizer used for double base rocket propellants. Both TEGDN and DEGDN (diethylene glycol dinitrate, 57 percent oxygen) were extensively studied. BDNPA/F (50 percent oxygen), a 1-1 eutectic of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl) formal, was similarly studied.

## C CURING AGENTS

Curing agents studied were selected primarily for oxygen content, wettability, and cure behavior. In addition to XF-4012 (approximately 30 percent oxygen), others studied were MA (maleic anhydride, 49 percent oxygen), ethylene glycol (52 percent oxygen), maleic half-esters of various polyols (approximately 40 to 45 percent oxygen), EC-MA [1-1 eutectic of ethylene carbonate and maleic anhydride (51 percent oxygen)],

and catalytic quantities of non-oxygen containing benzyldimethylamine (BDMA) and D.E.H.<sup>®</sup> 24 (triethylenetetramine). These represent the anhydride and amine type curing agents generally used with epoxy resins.

### SECTION III

#### EXPERIMENTAL RESULTS ON PLASTICIZED COMPOSITIONS

##### A PROCEDURES

The following procedures were used, unless specified otherwise in the report:

1. Sodium nitrate - Powdered Davies  $\text{NaNO}_3$  was ground in a Lee attrition mill, dried at least 16 hours at  $80^\circ\text{C}$ , reground, screened through 400 mesh sieve, and redried.
2. Magnesium - Atomized Valley Metallurgical Mg powder was used in three particle distributions. Initially a bimodal 50/100-100/200 mesh Mg was used, then a trimodal 30/50-50/100-100/200 mesh material, and finally 40/200 mesh Mg. Most of the work reported was done with two different batches of 40/200 mesh material (see Section VIII for mesh analyses).
3. TEGDN - Propellex, no inhibitor.
4. Mixing - Two different mixing techniques were employed. All initial work was done with a KitchenAid® Model K5-A mixer, wire whip blade at minimum speed. (Add epoxy resin, curing agent, TEGDN, and Mg; mix 3 to 5 minutes; add  $\text{NaNO}_3$ ; mix 5 minutes.) When optimization experiments were begun, it was found that this technique led to poor viscosity reproducibility. Therefore, the following procedure was adopted, using the Hamilton Beach Model 30 mixer: Add epoxy resin, curing agent and plasticizer; mix 1 to 2 minutes; add  $\text{NaNO}_3$ ; mix 5 to 10 minutes; add Mg; mix 10 to 15 minutes. Batches of 420 to 650 g. were prepared.
5. Fluidity - The viscosity was determined on an aliquot sample of the mix, at  $25^\circ\text{C}$ , using Brookfield RVF viscometer with T-type spindle.
6. Casting - The composition was poured into a 6-inch plastic funnel and allowed to flow into the mold. Four to six candles (103 to 107 g.) were prepared per batch.
7. Mold - A 1-1/4-inch ID x 4-inch long cardboard tube was lined with polyester film and plugged at the bottom with a No. 7 neoprene stopper. The mold was filled to a depth of 3.4 to 3.5 inches.
8. Curing - Candles were cured at  $70^\circ\text{C}$  for 16 to 40 hours.



9. Flare Case - The cured candle was removed from the mold, weighed and measured, reinserted into the mold, and an epoxy-sand plug was cast and cured at 20°C on the top (uppermost during casting) surface. Candles were removed from the mold, sprayed with Sprayon No. 321 aerosol paint for case-bonding and spirally wrapped (bifilarly) with Crystal Bay (2-inch width) masking tape. About one inch of extra case was left at the top for the igniter. Two wrapping methods were employed. In all initial work the tape was overlapped a half width during winding, resulting in a 4-ply case. This was found to reduce luminous efficiency. Therefore, for all flares fired after the beginning of the optimization program, a very small overlap of tape was used, resulting essentially in a 2-ply case.
10. Density - Density was determined geometrically from the weight and measured size of the candle.
11. Igniter - Two different starter mixtures were used. No difference in flare performance was noted due to ignition mix. Initially, the following composition was mixed, cast, and cured:

49.0% Mg, half 50/100, half 100/200 mesh  
27.0%  $\text{NaNO}_3$ , -400 mesh  
8.4% XFS-4008L  
6.0% XF-4012  
9.6% TEGDN

A powder was made by sawing the candle. From 0.25 to 0.75 g. of powder was placed on the top of the candle (lowermost end during casting), a length of igniter cord was added, and the excess tape case was twisted around it. In later work, the following composition was mixed, cast, and cured as a 0.5 g. igniter pellet attached to a length of igniter cord.

11.8% Mg, 100/200 mesh  
54.0%  $\text{KClO}_3$ , class 7  
19.8% XF-4013L  
12.6% MA  
1.8% PGNC

12. Attitude - The candles were burned vertically, ignited on the upper surface. Air flow was upward.
13. Flare Tunnel - The flares were fired in an 18-foot, 8-inch deep by 10-foot 5-inch wide by 10-foot 4-inch high concrete block hearth. The bottom of the flare was 4 feet, 9 inches above the floor. Ventilation was accomplished by an inlet in the floor below the flare and an external 2-speed blower in the roof above the flare. The flare tunnel itself, connected

to the hearth by a 4 by 9-foot doorway, is 60 feet long by 10 feet 5 inches wide by 14 feet high. The interior of the hearth and tunnel are painted black.

14. Light Measurement - Two Weston Model 856 YYV selenium photovoltaic cells are positioned 51.95 feet and 62.57 feet from the flare, at heights above the floor of 5.1 and 5.5 feet. The outputs of the photocells are amplified by Kintel Model 11BF amplifiers. Light output is recorded on a Honeywell Model 906B Visicorder oscillograph. A Dymec Model 2210 voltage-to-frequency converter and a Hewlett Packard Model 523 CR electronic counter are used to integrate the light output and record the integrated luminosity. The photocell is standardized with a General Electric Lamp No. 1M/T20BP, which at a constant voltage and amperage yields a specific horizontal candle-power.
15. Burning Time - Time of functioning was determined visually with a stop watch.
16. Replications - At least four candles were fired for each data point except where noted.

## B EXPERIMENTAL RESULTS

### 1. Effect of Nitrate Plasticizers on Combustion Behavior

Because of the dramatic effect of nitro-plasticizers on luminous efficiency (Table I), research was initiated to determine the maximum plasticization limits of energetic high oxygen plasticizers in gumstocks containing various binder systems.

### 2. Plasticizer Tolerance

The maximum compatibility level was visually ascertained by observing the surface wetness after curing for 16 hours at 70°C. As seen in Table II, nitrate plasticizers proved to be incompatible with XFS-4008L - ethylene glycol - BDMA, DGC - XF-4012, and DGC - D.E.H.<sup>®</sup> 24 binder systems. It is also evident that DGC accepts more plasticizer than XFS-4008L in the presence of an anhydride curing agent. D.E.H.<sup>®</sup> 24-cured XFS-4008L accepts the least plasticizer in this series. Finally, there appears to be no fixed order of plasticization limit for nitro-plasticizers.

### 3. Properties of Complete Flare Compositions

Studies were undertaken on nitro-plasticizer - compatible binder systems in complete flare compositions (Table III). Emphasis was placed first on learning the safety limitations of each composition at maximum plasticizer level from a small,

relatively safe mix of 10.0 g. Safe mixtures were later scaled to larger 650.0-g. mixes for actual flare production and evaluation. Thus, Table III includes impact and spark sensitivities obtained on 10-g. mixes, as well as viscosities and combustion behavior of flares prepared from the 650.0 g. batches.

TABLE I. EFFECT OF PLASTICIZER CONTENT ON LUMINOUS EFFICIENCY AND BURNING RATE

Composition (Percent)		
49.0 - Magnesium, bimodal 125 $\mu$ and 200 $\mu$		
27.0 - NaNO <sub>3</sub>		
24.0 - Binder - 58.3: 41.7, XFS-4008L:XF-4012		
TEGDN in Binder (Percent)	Luminous Efficiency (Cd-sec/g)	Burning Rate (In/sec)
40.0	53,000	0.037
30.0	36,000 <sup>a</sup>	0.036 <sup>a</sup>
20.0	21,300 <sup>a</sup>	0.039 <sup>a</sup>
10.0	14,000 <sup>a</sup>	0.038 <sup>a</sup>
<sup>a</sup> Single candles.		

All compositions tested showed adequate resistance to impact and spark hazards.

An unfavorable combination of high viscosity and low luminous efficiency is displayed by compositions containing maleic half esters of polyols. Additionally, doming and swelling during cure disqualified this binder system from further work. Surprisingly, the DGC - EC-MA binder system, one of highest in oxygen content, registered low efficiency and rapid burning rate. However, poor grain integrity, due to very high viscosity and poor wettability, probably is responsible. The DGC - MA - TEGDN composition also displays an unexpectedly high viscosity, increased burning rate, and low efficiency. These poor results are undoubtedly due to the shelf instability of DGC.

TABLE II. PLASTICIZER TOLERANCE OF VARIOUS BINDER SYSTEMS

Binder	Binder/Curing Agent Ratio	Plasticizer	Plasticizer Limit (Percent)
XFS-4008L XF-4012	58.3/41.7	TEGDN DEGDN BDNPA/F	40-45.0 50-55.0 65-70.0
XFS-4008L - MA	58.8/41.2	TEGDN DEGDN BDNPA/F	50-55 45-40 40-45
XFS-4008L - EC-MA	41.6/58.4	TEGDN DEGDN BDNPA/F	35-40 40-45 30-35
XFS-4008L - Ethylene glycol - BDMA	78.7/17.1/4.2	TEGDN BDNPA/F	No cure Violent decomposition
XFS-4008L - D.E.H. <sup>®</sup> 24	97.0/3.0	TEGDN DEGDN BDNPA/F	30-35 35-40 30-35
DGC - XF-4012	46.8/53.2	All	No cure
DGC - MA	47.3/52.7	TEGDN DEGDN BDNPA/F	55-60 55-60 45-50
DGC - EC-MA (1-1)	31.0/69.0	TEGDN DEGDN BDNPA/F	50-55 50-55 35-40
DGC - D.E.H. <sup>®</sup> 24	78.6/21.4	All	Violent decomposition

The most promising plasticized binder systems, on the basis of lowest viscosities and highest efficiencies, were the XFS-4008L - EC-MA, XFS-4008L - MA, XFS-4008L - D.E.H.<sup>®</sup> 24, and XFS-4008L - XF-4012 compositions.

Since the viscosities shown in Table III are below that required for pour castability, these systems were excellent candidates for optimization studies at reduced binder levels, where increased luminous efficiencies can be anticipated. An indication of pour castability, using 24% binder level, is shown in Figure 1.

TABLE III. GENERAL PROPERTIES OF COMPLETE<sup>a</sup> FLARE COMPOSITIONS

XFS-100BL (%)	DOC (%)	XF-1012 (%)	MA (%)	EC-MA (%)	D.E.H.® 24 (%)	BONPA/F (%) in Binder	TEGDN (%) in Binder	DECHN (%) in Binder	Binder (%) Oxygen	Viscosity (cps) 25°C.	Impact <sup>c</sup> Eso (Kg. cm)	Density (g/cc)	Luminous Efficiency (Cd-sec/g)	Burning Rate (in./sec)
8.4		6.0				40.0			39.5	775,000	300+	1.44	29,400	0.061
4.9		3.5				65.0			45.3	874,000	300		24,000 <sup>d</sup>	0.053
8.4		6.0					40.0		40.6	115,000		1.70	31,000 <sup>d</sup>	0.051
7.0		5.0					50.0		45.9	100,000	300	1.50	31,700 <sup>e</sup>	0.052
8.4		6.0						40.0	43.8	300,000	300+		28,000 <sup>d</sup>	0.054
8.5			5.9			40.0			44.9	125,000	105	1.74	33,800 <sup>d</sup>	0.057
7.2			7.2				40.0		46.1	75,000		1.60	29,500 <sup>d</sup>	
6.0			6.0				50.0		46.6	250,000	275	1.51	36,400	0.060
7.8			5.4					45.0	49.1	55,000	225	1.62	34,200 <sup>d</sup>	0.069
7.0				9.8		30.0			46.4	250,000	200	1.53	37,300	0.062
6.5				9.1			35.0		47.3	100,000	190	1.58	40,500	0.060
6.0				8.4				40.0	50.7	142,000	177	1.58	44,500	0.069
16.3					0.5		30.0		39.0	190,000	300+	1.59	30,900	0.051
15.1					0.5			35.0	42.1	137,500	300+	1.57	31,400	0.069
4.8 <sup>b</sup>								35.0		1.6 x 10 <sup>6</sup>	300+	1.19	24,900	0.082
	6.2		7.0			45.0			49.2	165,000	230	1.57	36,000 <sup>d</sup>	0.067
	5.1		5.7				55.0		51.0	Too high	300	1.39	26,500	0.090
	5.1		5.7					55.0	54.7	42,000	100	1.67	32,700 <sup>d</sup>	0.073
	4.8			10.8		35.0				Too high	300+	1.36	29,000	0.101
	3.7			8.3			50.0		51.4	Dry	200	1.46	25,600	0.125
	3.7			8.3				50.0	54.8	Dry	220	1.51	29,300	0.092

<sup>a</sup>49.0% Magnesium - 27.0% NaNO<sub>3</sub> - 24% Binder. (40/200 mesh Mg, except as noted.)<sup>b</sup>This composition contained 10.8% half ester D.<sup>c</sup>Olin drop weight tester, 50 percent fire level. All compositions were also tested for spark sensitivity using the Dow electrostatic generator, open cup. None ignited at the highest setting, 18.75 joules.<sup>d</sup>One third each 30/50, 50/100, and 100/200 mesh Mg.<sup>e</sup>Half each 50/100 and 100/200 mesh Mg.



Figure 1. Consistency of Cast Flare Composition

In addition, while all cured grains exhibited sufficient hardness, MA-cured compositions appeared toughest and also highest in case-bonding strength.

#### 4. Surveillance

The composition containing the XFS-4008L - XF-4012 - TEGDN binder system was studied extensively for storage surveillance stability at 70°C (Table IV).

The data indicate an adequate degree of thermal stability for three levels of plasticizer after 12 weeks exposure at either ambient conditions or 70°C.

The flare candles contained 49 percent trimodal Mg, 27 percent  $\text{NaNO}_3$  (-400 mesh), and 24 percent binder. The ratio of XFS-4008L to XF-4012 was 1.4, and the plasticizer was varied from 20 to 40 percent of the binder.

A comparison of various binder systems after four weeks surveillance at 70°C is shown in Table V. The XFS-4008L - XF-4012 - TEGDN binder composition is included for comparative purposes.

Because of relatively high weight loss and poor physical appearance, no further work was done on BDNPA/F. Similarly, rapid burning and questionable shelf-life contributed to suspension of further work with DGC. The remaining systems, XFS-4008L - XF-4012, XFS-4008L - MA, XFS-4008L - D.E.H.<sup>®</sup>-24, and XFS-4008L - EC-MA, plasticized with either TEGDN or DEGDN, continued to be desirable candidates for optimization studies.

TABLE IV. RESULTS OF HIGH TEMPERATURE STORAGE

TEGDN Plasticizer Level (Percent)	Initial	12 Weeks (Ambient)	4 Weeks (70°C)	8 Weeks (70°C)	12 Weeks (70°C)
<u>Luminous Efficiency (Cd-sec/g)</u>					
40	31,000	28,400	25,900	26,600	26,300
30	22,000	22,900	21,500	20,100	20,000
20	16,500	16,500	16,700	15,100	15,130
<u>Burning Rate (In/sec)</u>					
40	0.051	0.050	0.062	0.049	0.047
30	0.049	0.050	0.060	0.050	0.049
20	0.049	0.050	0.053	0.051	0.050
<u>Weight Loss (Percent)</u>					
40		(0.02) <sup>a</sup>	0.17	0.43	0.36
30		(0.02) <sup>a</sup>	0.10	0.34	0.34
20		(0.11) <sup>a</sup>	0.08	0.16	0.18
<sup>a</sup> Weight gain.					

TABLE V. COMPARATIVE SURVEILLANCE RESULTS

Resin (%)	Curing Agent (%)	TEGDN (%)	DEGDN (%)	BDMPA/F (%)	Weight Loss 4 wks. 70°C (%)	Luminous Efficiency (cd sec/g)		Burning Rate (in/sec)	
						Initial	4 Weeks	Initial	4 Weeks
XFS-4008L	FP-4012								
8.4	6.0	9.6(40 <sup>a</sup> )	--	--	0.17	31,000 <sup>b</sup>	25,900	0.052	0.062
7.0	5.0	--	12.0(50 <sup>a</sup> )	--	0.34	31,700	39,500	0.052	0.062
8.4	6.0	--	--	9.6(40 <sup>a</sup> )	2.20	29,400	19,900	0.064	0.064
XFS-4008L	MA								
6.0	6.0	12.0(50 <sup>a</sup> )	--	--	1.42	36,400	42,300	0.061	0.061
7.8	5.4	--	10.8(45 <sup>a</sup> )	--	0.98	34,200 <sup>b</sup>	34,500	0.069	0.070
8.5	5.9	--	--	9.6(40 <sup>a</sup> )	1.51	33,800 <sup>b</sup>	35,500	0.057	0.076
XFS-4008L	D.E.H. 24								
16.3	0.5	7.2(30 <sup>a</sup> )	--	--	(0.27 <sup>c</sup> )	30,900	35,700	0.051	0.051
15.1	0.5	--	8.4(35 <sup>a</sup> )	--	0.02	31,400	34,700	0.069	0.059
XFS-4008L	EC-MA								
6.5	9.1	8.4(35 <sup>a</sup> )	--	--	0.84	40,500	39,200	0.060	0.059
6.0	8.4	--	9.6(40 <sup>a</sup> )	--	3.76	44,500	36,500	0.069	0.068
7.0	9.8	--	--	7.2(30 <sup>a</sup> )	1.77	37,300	35,300	0.062	0.059
DGC	EC-MA								
3.7	8.3	12.0(50 <sup>a</sup> )	--	--	0.52	25,500	37,000	0.125	0.072
3.7	8.3	--	12.0(50 <sup>a</sup> )	--	0.38	29,300	40,300	0.092	0.065
4.8	10.8	--	--	8.4(35 <sup>a</sup> )	1.32	23,000	34,400	0.101	0.093
DGC	MA								
5.1	5.7	13.2(55 <sup>a</sup> )	--	--	0.62	26,500	42,900	0.090	0.070
5.1	5.7	--	13.2(55 <sup>a</sup> )	--	0.24	32,700 <sup>b</sup>	34,600	0.073	0.063
6.2	7.0	--	--	10.8(45 <sup>a</sup> )	0.21	36,000 <sup>b</sup>	33,500	0.067	0.066
XFS-4008L	Half Ester D								
4.8	10.8	--	8.4(35 <sup>a</sup> )	--	(0.84 <sup>f</sup> )	24,900	32,600	0.082	0.073

<sup>a</sup>% Plasticizer in binder.<sup>b</sup>Trimodal Mg blend. Others listed contain 40/200 Mg.<sup>c</sup>Weight gain.



SECTION IV  
OPTIMIZATION

A VISCOSITY REPRODUCIBILITY

To conduct meaningful optimization studies, effective control of castability is necessary. Initial attempts to reproduce the original viscosity of a XFS-4008L - EC-MA - DEGDN flare composition gave 400,000 cps, considerably higher than the original 142,000 cps. Reducing the binder content to 23.0 percent produced a viscosity in excess of  $1.0 \times 10^6$  cps. The same effect was found for the XFS-4008L - MA flare composition. Therefore, considerable effort was directed toward learning the cause of the inconsistency.

Since it seemed likely that moisture pickup, due to high humidity, was responsible, freshly prepared EC-MA eutectic was tried with no improvement. Fresh MA from an alternate source also gave a high viscosity. Coarse  $\text{NaNO}_3$ , -200 mesh also gave poorer castability. However, freshly prepared -400 mesh  $\text{NaNO}_3$  gave a mix with 150,000 cps viscosity. The problem appeared to be caused by a tendency for agglomeration of the  $\text{NaNO}_3$ , aggravated by atmospheric humidity.

It was found that maximum dispersion of non-agglomerated  $\text{NaNO}_3$  was necessary. Potential dispersing techniques investigated were high-shear pre-dispersion and use of the anticaking agents MgO and Cab-o-sil M-S (Table VI).

Using a high-shear Hamilton Beach Model 30 blender for pre-dispersing freshly ground  $\text{NaNO}_3$  (-400 mesh) with XFS-4008L, DEGDN, and EC-MA produced a very fluid dispersion. Incorporation of the final component, 40/200 mesh magnesium, produced a very castable flare composition having a viscosity of 87,500 cps at 25°C. Similarly, high-shear pre-dispersion of  $\text{NaNO}_3$  containing 0.37 percent MgO in XFS-4008L, TEGDN, and finally with MA yielded a final composition viscosity of 117,500 cps at 25°C. The high luminous efficiency and burning rate typical of the EC-MA - XFS-4008L - DEGDN binder system was obtained by this modified mixing technique. Grain height increased approximately 10 percent during cure, however, and grain structure indicated a high retention of entrapped air due to the high-shear mixing.

High-shear pre-dispersion of  $\text{NaNO}_3$  was adopted for all optimization work. The use of MgO and Cab-o-sil was also adopted for storage of ground  $\text{NaNO}_3$  to prevent caking; 0.50 percent MgO and 0.25 percent Cab-o-sil M-S were added to the pan before screening and the  $\text{NaNO}_3$  was screened into these additives.

TABLE VI. EFFECT OF SODIUM NITRATE PRE-DISPERSION

Composition	No. 1	No. 2
Magnesium, 40/200 (Percent)	49.0	49.0
NaNO <sub>3</sub> , -400 mesh (Percent)	27.0	27.0 <sup>a</sup>
XFS-4008L (Percent)	6.0	7.06
EC-MA (Percent)	8.4	--
MA (Percent)	--	4.94
DEGDN (Percent)	9.6	--
TEGDN (Percent)	--	12.00
Viscosity (cps, 25°C)	87,500	117,500
Luminous Efficiency (cd-sec/g)	57,000	59,400
Burning Rate (in/sec)	0.081	0.058
<sup>a</sup> Includes 0.37 Percent MgO.		

## B CASE STUDY

Luminous efficiencies measured for cast flares during the initial part of this effort were consistently lower (20 to 40 percent) than results obtained on a previous effort for Picatinny Arsenal. Firings with standard pressed flares established that performance results measured in the Dow Larkin Laboratory flare tunnel are substantially the same as those obtained at the old 655 Building facility. However, it was discovered that the manner of wrapping the flare candles with paper tape was changed between the two programs. In both cases, two wrappings of two-inch Crystal Bay masking tape have been spirally wrapped (bifilarly) on the candle. However, previous practice was to overlap each course of tape only enough to prevent flare propagation down the spiral gap, resulting essentially in two plies of tape on the candle. The changed practice was to overlap the tape about half of its width, resulting in a four-ply paper tape case.

Standard pressed flares containing Mk 45 composition were fired with both types of taped case. The four-ply configuration gave an efficiency of 60,300 cs-sec/g and a burning rate of 0.061 in/sec; a two-ply tape case gave 71,200 cs-sec/g and 0.060 in/sec.

Because of these results, a study was undertaken to determine the best way to inhibit side burning on research flare candles with minimum deleterious effect on performance. The XFS-4008L - EC-MA - TEGDN (35 percent) binder system was chosen for this study. Flares were encased in various ways and functioned (Table VII).

For the taped flare candles, Crystal Bay, Mystic, Scotch, and Ethocel<sup>a</sup> tapes appeared to be satisfactory. The four-ply wrappings reduced efficiency, probably by forming chimneys. The two-ply and one-ply wrappings appeared equivalent, except possibly in the case of Ethocel<sup>a</sup>, which had some efficiency loss. There was visual evidence of some side burning for the one-ply paper tape cases.

For the inhibiting coatings, which were applied by spraying, dipping, or brushing, side burning was prevented only when the XFS-4008L - D.E.H.<sup>®</sup> 24 resin, loaded with magnesium powder, was used. The presence of Mg in the case may account for the unusually high efficiency.

The following cases were deemed satisfactory: two-ply Crystal Bay tape, two-ply Mystic tape, two-ply Scotch<sup>®</sup> masking tape, and one-ply Ethocel<sup>®</sup> tape. Because of previous experience and minor advantages, the two-ply Crystal Bay case was chosen for all optimization work.

#### C DOMING AND GRAIN EXPANSION

Different experience with doming and surveillance between Dow and Picatinny Arsenal prompted a joint investigation of the nitro-plasticized XFS-4008L - EC-MA and XFS-4008L - XF-4012 flare compositions. The formulations shown in Table VIII were prepared and cast into epoxy-lined aluminum "Trip Flare" cases (1.50-inch OD, 1.39-inch ID, 4-inch depth) for surveillance studies at Picatinny Arsenal.

All compositions produced flowable, castable mixes. Upon curing, severe frothing and doming occurred in the EC-MA cured composition. Deaeration eliminated frothing, but doming persisted. Further, extensive drying of all ingredients failed to show a significant improvement. A promising solution was the addition of 0.5 percent MgO and 0.25 percent Cab-o-sil to the NaNO<sub>3</sub>. This was sufficient to assure elimination of grain expansion and to facilitate maximum dispersion of the NaNO<sub>3</sub>. This gassing reaction with 10.0 percent XFS-4008L and 6.8 percent EC-MA present did not occur in a stoichiometric mix (7.0 percent XFS-4008L, 9.8 percent EC-MA), and future work should be limited to such mixes.

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<sup>a</sup>Ethocel, a trademark of The Dow Chemical Company for ethylcellulose resin.

TABLE VII. FLARE CASE STUDY RESULTS

Case Type	Luminous Efficiency (Cd-sec/g)	Burning Rate (In/sec)
Tape		
4-Ply Crystal Bay paper tape <sup>a</sup>	38,800	0.059
4-Ply Mystic paper tape <sup>a</sup>	44,700	0.055
2-Ply Crystal Bay paper tape <sup>a</sup>	56,600	0.051
2-Ply Mystic paper tape <sup>a</sup>	59,600	0.054
1-Ply Crystal Bay paper tape <sup>a</sup>	57,500	0.052
1-Ply Mystic paper tape <sup>b</sup>	56,100	0.059
1-Ply Scotch <sup>®</sup> masking tape <sup>c</sup>	56,800	0.055
1-Ply PVC tape <sup>c</sup>	33,500	0.074
1-Ply rubber tape <sup>c</sup>	42,600	0.050
1-Ply acetate filament tape <sup>c</sup>	47,700	0.049
2-Ply Ethocel <sup>®</sup> tape <sup>c</sup>	49,900	0.047
1-Ply Ethocel <sup>®</sup> tape <sup>c</sup>	56,200	0.050
Inhibiting Coatings		
Sprayon <sup>®</sup> #321 gray primer paint <sup>c</sup>	50,100	0.129
Sprayon <sup>®</sup> #321 acrylic lacquer topcoat <sup>c</sup>	58,700	0.093
DL 308 Intumescent paint <sup>c</sup>	40,300	0.079
Hetron <sup>®</sup> polyester <sup>c</sup>	51,600	0.085
Saran <sup>®</sup> lacquer <sup>c</sup>	57,800	0.110
XFS-4008L - D.E.H. <sup>®</sup> 24 <sup>c</sup>	59,400	0.089
XFS-4008L - D.E.H. <sup>®</sup> 24 - Mg (50%) <sup>c</sup>	68,100	0.053
XFS-4008L - D.E.H. <sup>®</sup> 24 - D.E.R. <sup>®</sup> 542 <sup>c</sup>	49,400	0.061
<sup>a</sup> Four candles fired.		
<sup>b</sup> Two candles fired.		
<sup>c</sup> One candle fired.		

TABLE VIII. TRIP FLARE COMPOSITIONS

Formulations	1 Percent	2 Percent	3 Percent
Magnesium, 30/50	--	49.0	49.0
Magnesium, 50/100	24.5	--	--
Magnesium, 100/200	24.5	--	--
NaNO <sub>3</sub> , <400 mesh	27.0	27.0	27.0
XFS-4008L	9.80	10.0	16.3
XF-4012	7.0	--	--
EC-MA	--	6.8	--
D.E.H. <sup>®</sup> 24	--	--	0.5
TEGDN	7.2	7.2	7.2

## D XFS-4008L - EC-MA - DEGDN SYSTEM

Figure 2 shows the effects of magnesium to sodium nitrate ratio and binder content on viscosity for XFS-4008L - EC-MA - DEGDN compositions. The 49/27 Mg/NaNO<sub>3</sub> ratio appears well optimized for maximum castability, displaying minimal viscosity over the ranges of 21.4 to 24 percent binder. The 49/27 Mg/NaNO<sub>3</sub> ratio and approximately 21.2 percent binder level should yield about 500,000 cps viscosity. Optimization results for XFS-4008L - EC-MA - DEGDN compositions are given in Table IX. The unfavorable effect of increased binder content on luminous efficiency and burning rate is apparent. Interpolating from the data at 21 and 22 percent binder for this composition, a luminous efficiency of approximately 66,000 cd-sec/g at a burning rate of about 0.065 in/sec would be predicted. However, study of the actual composition produced an unexpectedly low efficiency of 61,600 cd-sec/g and a burning rate of 0.056 in/sec. Because of this, and because some other data points do not fall on smooth curves, reinvestigation is in order.

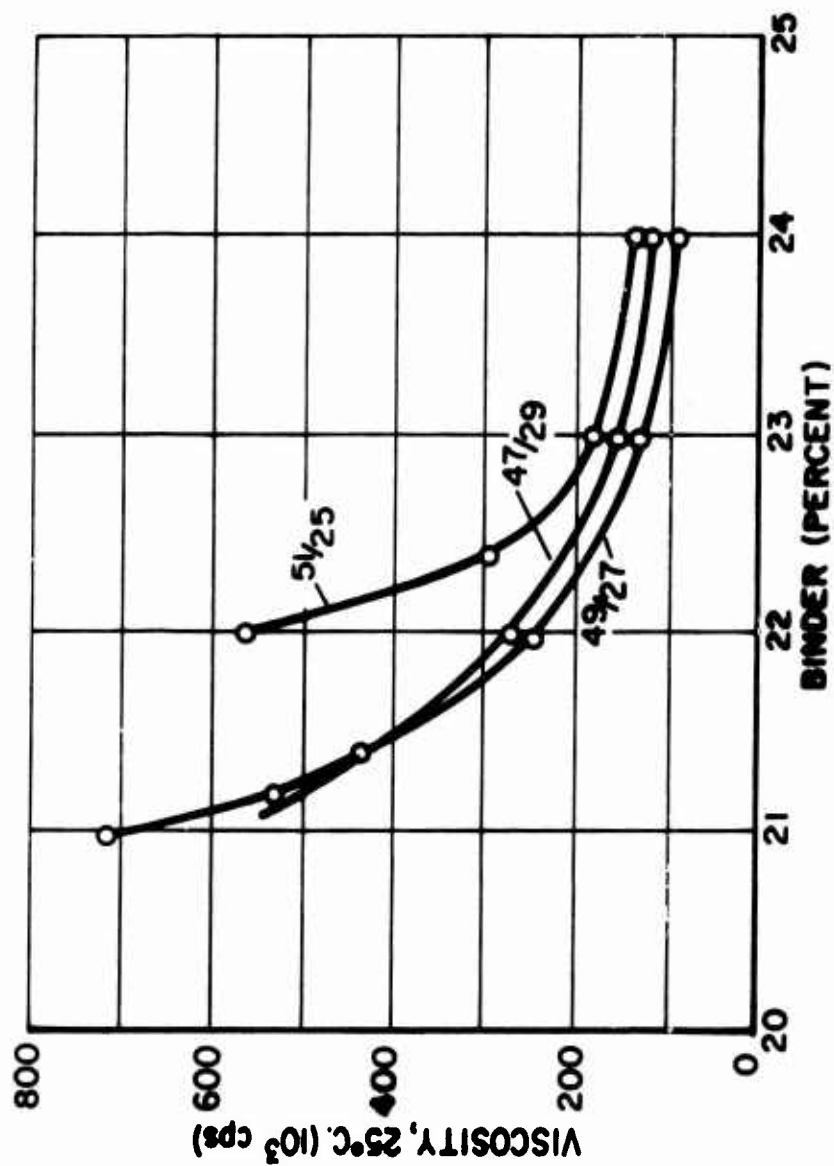


Figure 2. Effects of Binder Content and Magnesium/Sodium Nitrate Ratio on Viscosity (XFS-4008L - EC-MA - DEGDN)

TABLE IX. OPTIMIZATION STUDIES OF COMPOSITIONS  
CONTAINING XFS-4008L - EC-MA - DEGDN BINDER<sup>a</sup>

Binder (%)	Mg <sup>b</sup> /NaNO <sub>3</sub> Ratio	Viscosity (cps)	Luminous Efficiency (cd-sec/g)	Burning Rate (in/sec)	Density (g/cc)
24.0	47/29	127,500	56,400	0.0480	1.64
24.0	49/27	87,000	50,000	0.0550	
24.0	51/25	130,000	55,400	0.047	1.59
23.0	47/29	155,000	60,000	0.048	1.62
23.0	49/27	132,500	50,500	0.0567	1.61
23.0	51/25	175,000	54,900	0.047	1.61
22.0	45/31	315,000	52,200	0.0514	1.66
22.0	47/29	265,000	57,700	0.0517	1.66
22.0	49/27	245,000	61,000	0.0600	1.61
22.0	51/25	563,000	70,000	0.0563	1.59
22.0	53/23	712,500	61,800	0.0505	1.57
22.4	51/25	290,000	58,800	0.049	1.58
21.4	47/29	437,500	62,000	0.051	1.65
21.2	49/27	525,000	60,600	0.0564	1.62
21.0	49/27	712,500	66,900	0.0646	1.60
<sup>a</sup> XFS-4008L:EC-MA:DEGDN = 6.0:8.4:9.6					
<sup>b</sup> 40/200 mesh Mg					

The completed optimization study at 22 percent binder shows that maximum burning rate and minimum viscosity occur at the 49/27 Mg/NaNO<sub>3</sub> ratio (Figure 3). However, the highest efficiency (70,000 cd-sec/g) was obtained at a Mg/NaNO<sub>3</sub> ratio of 51/25 and binder content of 22 percent. For this composition the viscosity should approach 500,000 to 600,000 cps at room temperature, and the burning rate, 0.056 in/sec. This appears at present to be the best composition for this binder system.

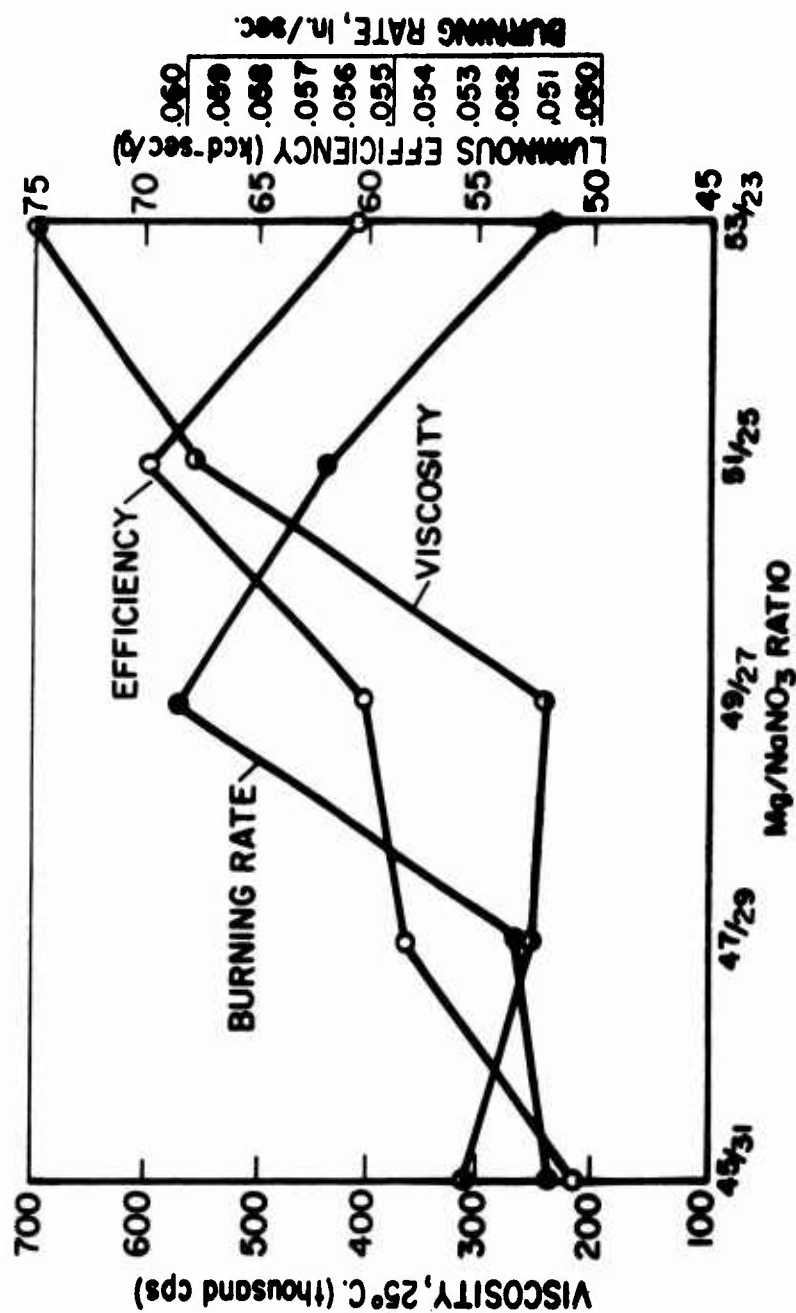


Figure 3. Effect of Magnesium/Sodium Nitrate Ratio on Viscosity and Combustion Behavior (XFS-4008L - EC-MA - DEGDN)



#### E. XFS-4008L - MA - TEGDN AND XFS-4008L - XF-4012 - DEGDN

Optimization results for compositions containing the XFS-4008L - MA - TEGDN and XFS-4008L - XF-4012 - DEGDN binders are presented in Table X. The 49/27 magnesium/sodium nitrate ratio was utilized throughout this study.

As seen in Figure 4, compositions containing either MA or XF-4012 curing agents display the expected viscosity increase with reduced binder levels. The XF-4012 cured compositions show superior castability. While the MA system required 21.8 percent binder to attain 500,000 cps viscosity, only about 20.5 percent of the XF-4012 system should produce equivalent castability.

Some unusual and unexpected results, however, were obtained when the performance of these flares was evaluated for combustion behavior. The burning rate of XF-4012 cured compositions was found to decrease smoothly as binder level increases. For MA cured formulations, however, the burning rate at 23 percent binder is anomalously high. At equivalent binder levels, the MA-based flares burn 10 to 20 percent faster than those containing XF-4012.

As the binder level decreases, the luminous efficiency generally improves, as expected. However, for both MA and XF-4012 cured systems an anomalous low result was obtained at the lowest binder level studied.

Because of these puzzling results and because the Mg/ $\text{NaNO}_3$  ratio was not varied, these compositions must not be considered to be optimized for these binder systems. The data do indicate, however, significantly lower efficiencies for XF-4012 containing compositions at all binder levels.

#### F. "BEST EFFORTS" COMPOSITION

A comparison of optimization results at one Mg/ $\text{NaNO}_3$  ratio is presented in Figures 5, 6, and 7. Systems cured with XF-4012 have the lowest viscosity due to superior ability to wet the solid particles. Anhydride-cured systems appear to excel in luminous efficiency and, at the same time, have higher burning rates.

As a result of the optimization experiments, the following composition is recommended as a "best efforts" formula:

52% Mg (40/200)  
26%  $\text{NaNO}_3$  (<400 mesh)  
  
22%  $\left\{ \begin{array}{l} \text{XFS-4008L (25\%)} \\ \text{EC-MA (35\%)} \\ \text{DEGDN (40\%)} \end{array} \right.$

TABLE X. OPTIMIZATION STUDIES ON COMPOSITIONS<sup>a</sup>  
CONTAINING XFS-4008L - MA - TEGDN  
AND XFS-4008L - XF-4012 - DEGDN

Ingredient	%	Plasticizer <sup>b</sup>	Viscosity (cps, 25°C)	Density (G/cc)	Luminous Efficiency (Cd-sec/g)	Burning Rate (In/sec)
XFS-4008L - MA	24.0	TEGDN	135,000	1.63	54,000	0.052
XFS-4008L - MA	23.0	TEGDN	185,000	1.62	63,700	0.058
XFS-4008L - MA	22.0	TEGDN	410,000	1.62	52,600	0.056
XFS-4008L - MA	22.0	DEGDN	415,000	1.63	59,100	0.057
XFS-4008L - XF-4012	24.0	DEGDN	72,500	1.64	47,700	0.048
XFS-4008L - XF-4012	23.0	DEGDN	105,000	1.63	53,300	0.048
XFS-4008L - XF-4012	22.0	DEGDN	195,000	1.59	55,000	0.049
XFS-4008L - XF-4012	21.0	DEGDN	360,000	1.59	50,200	0.051
XFS-4008L - XF-4012 (800 gram-batch)	20.0	DEGDN	345,000	1.72	--	--
<sup>a</sup> Mg/NaNO <sub>3</sub> = 49/27 <sup>b</sup> 50.0 percent of Binder						

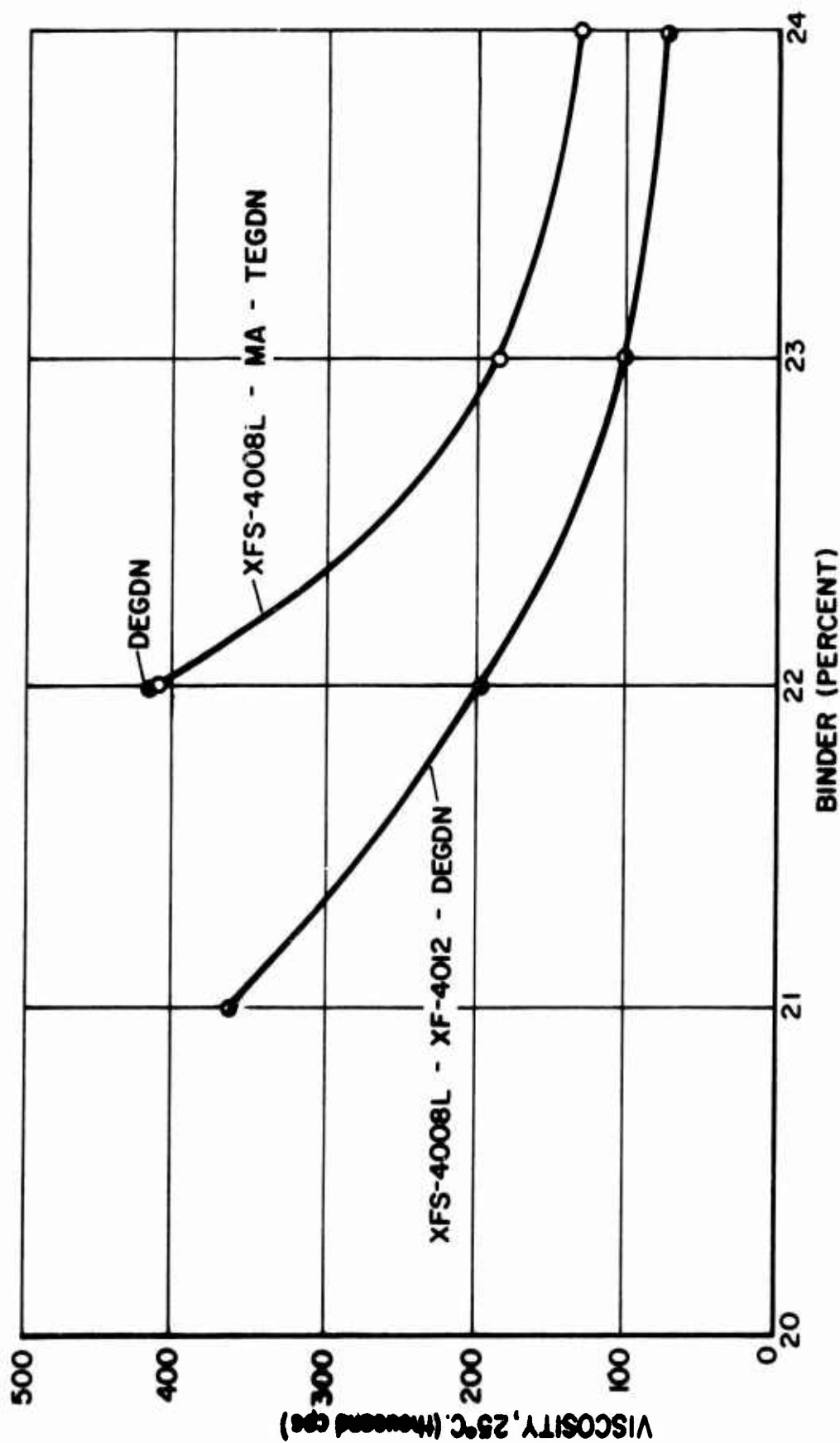


Figure 4. Effect of Binder Content on Viscosity

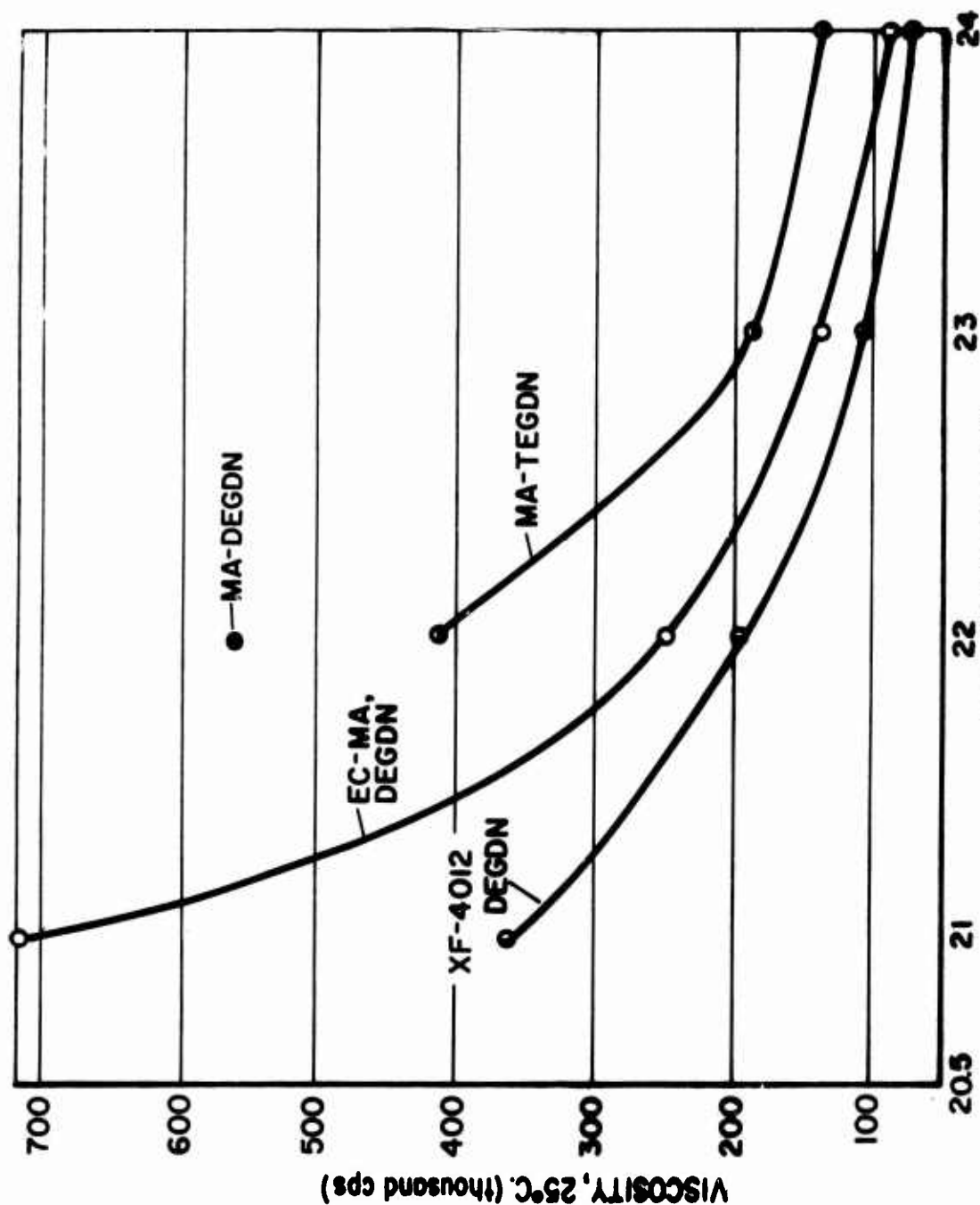


Figure 5. Comparative Effects of Binders on Mix Viscosity  
(49/27 Mg/NaNO<sub>3</sub> Ratio, XFS-4008L Resin)

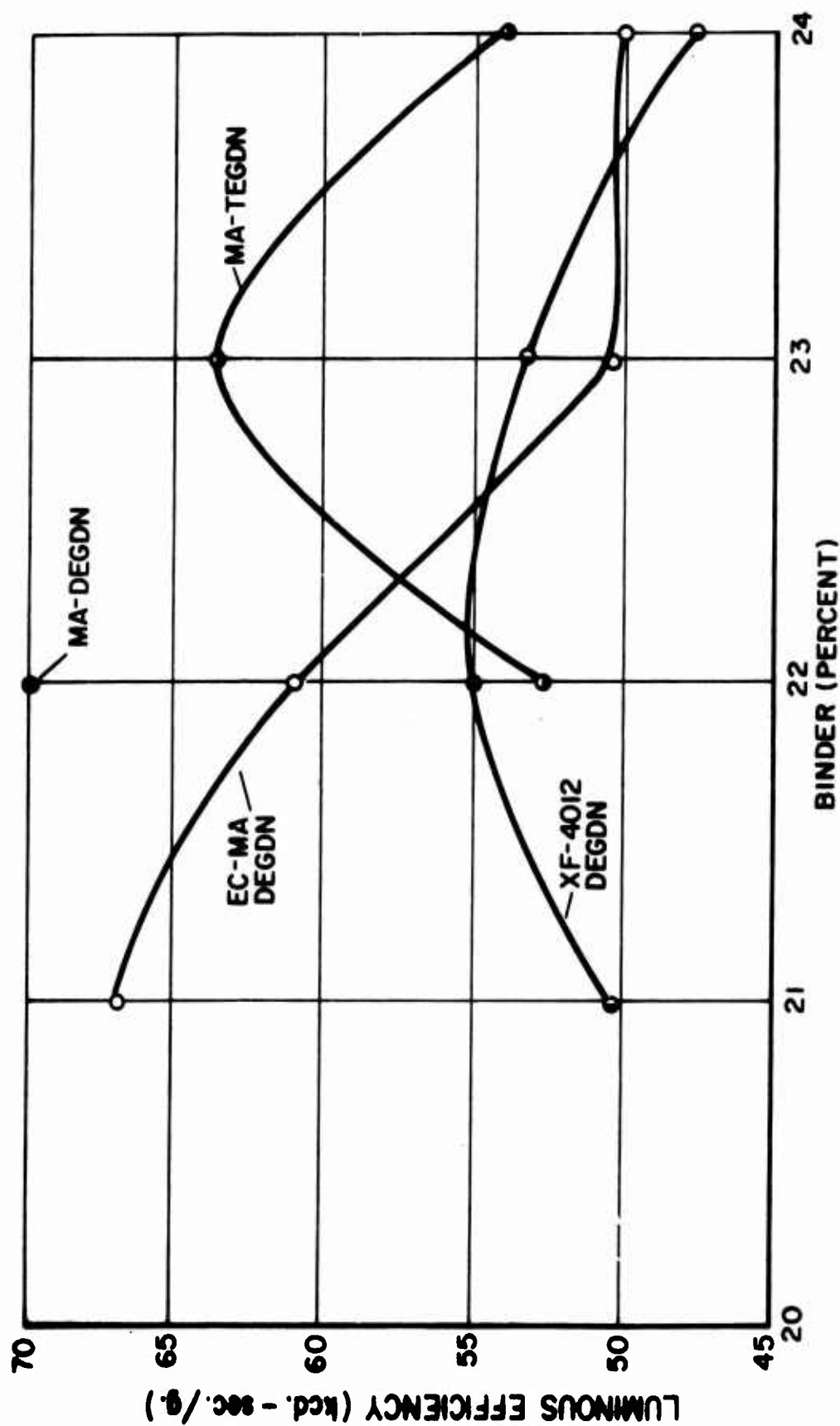


Figure 6. Comparative Effects of Binders on Luminous Efficiency (49/27 Mg/NaNO<sub>3</sub> Ratio, XFS-4008L Resin)

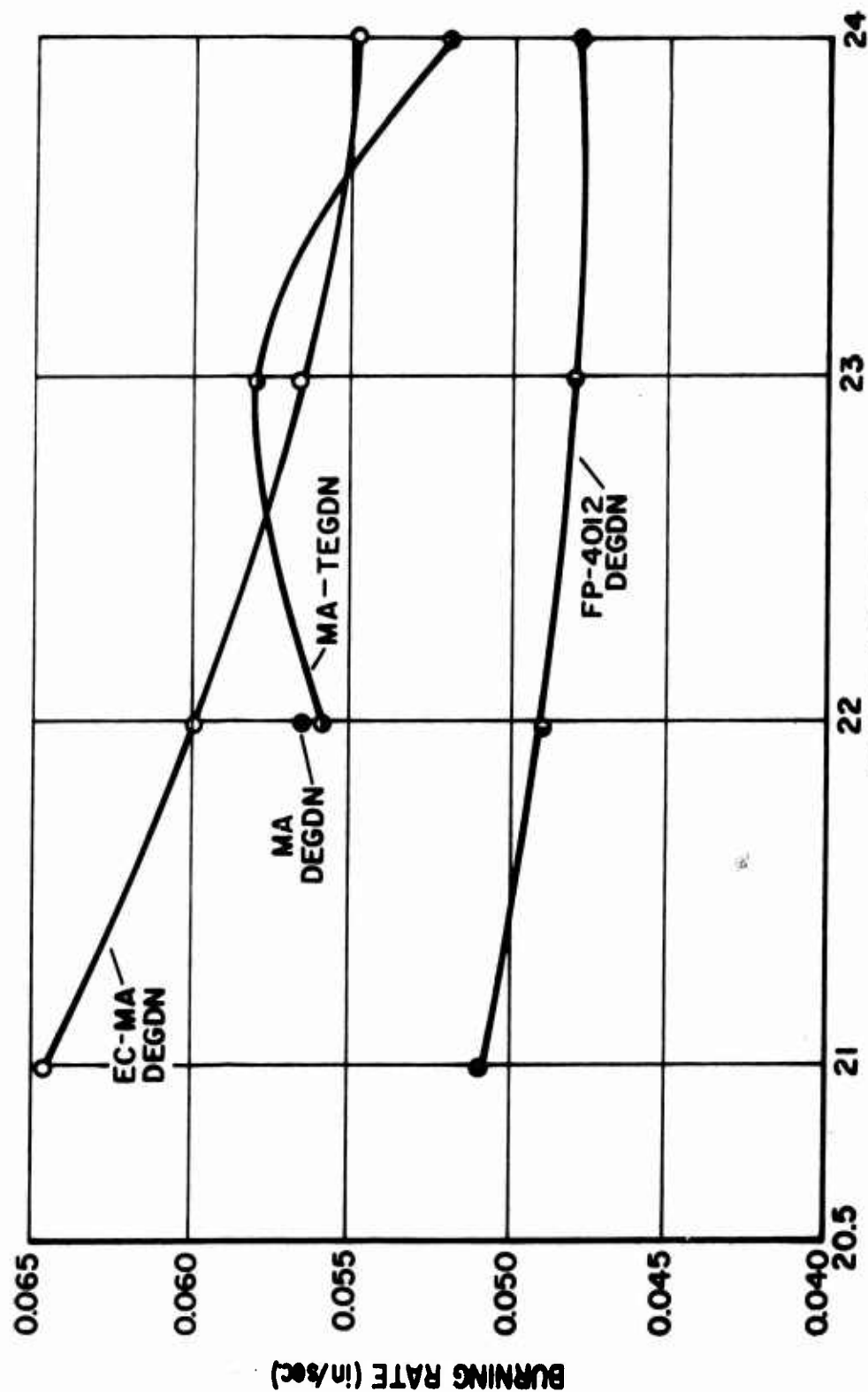


Figure 7. Comparative Effects of Binders on Burning Rate  
(49/27 Mg/NaNO<sub>3</sub> Ratio, XFS-4008L Resin)

Although the viscosity, 563,000 cps, slightly exceeds the goal of a maximum of 500,000 cps, it should be sufficiently castable to meet production requirements. The luminous efficiency obtained in 1.25-inch taped candles, 70,000 cd-sec/g, appears very satisfactory. The burning rate, 0.056 in/sec, is lower than for most pressed flare compositions. However, in a different case material, different diameter, and different orientation during burning, the compositions's burning rate undoubtedly will change.

Figure 8 shows a typical trace of light output obtained during the firing of this "best efforts" composition. The combustion appears to be smooth, the light output is steady, and fluctuation is less than  $\pm 10$  percent. There is no evidence of side burning.

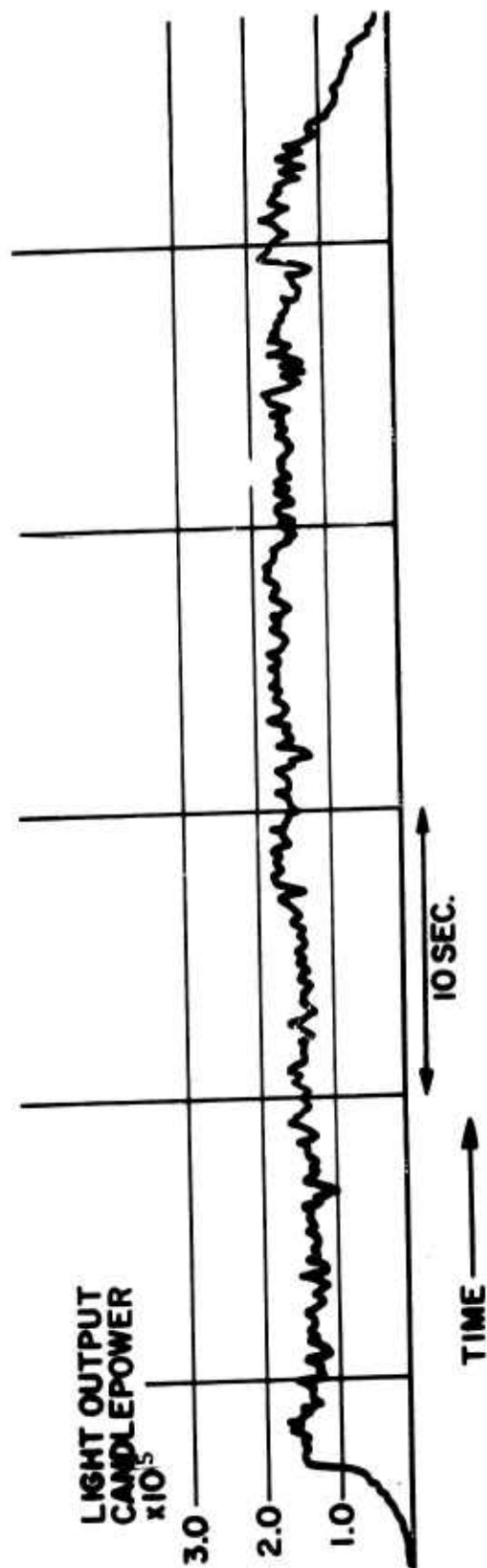


Figure 8. Light Output Trace From "Best Efforts" Composition  
(51/25 Mg/NaNO<sub>3</sub> Ratio, 22 percent XFS-4008L - EC-MA - DEGDN Binder)



## SECTION V

### LARGE DIAMETER FLARE AND EXOTHERM STUDY

An 800-g mix containing 21.4 percent of the XFS-4008L - EC-MA - DEGDN binder system and a Mg/NaNO<sub>3</sub> ratio of 47/29 produced a viscosity of 412,500 cps. A 3.2-inch-diameter x 4-inch-long candle was cast. It displayed a mild and easily controllable exotherm of 7.0°C for approximately 15 to 20 minutes. The cured flare (70°C , 20 hours) had a density of 1.63 and showed no evidence of expansion. The candle was tape wrapped and, upon combustion, a luminous efficiency of 59,600 cd-sec/g was obtained at a burning rate of 0.052 in/sec. This compares with the values of 62,000 cd-sec/g and 0.051 in/sec obtained in the 1.25-inch-diameter candles.

## SECTION VI

### COMPARATIVE MARK 45 COMPOSITION FIRINGS

In order that light output measurements could be related comparatively to known flare compositions, standardized pressed 1.25-inch-diameter candles containing composition used in Mark 45 flares were fired at frequent intervals in conjunction with firings of developmental flares. A total of 68 of these candles were tested. These candles, wrapped with a 4-ply tape case, consistently gave about 60,000 cd-sec/g average efficiency, except during the summer when higher values prevailed. During the early part of the program (February to April 1970) a spread of about  $\pm 10,000$  cd-sec/g for the individual candles in a group was noted, but the average performance remained constant. Later (May to October 1970) data showed a spread of about  $\pm 4,000$  cd-sec/g. The higher values in the summer (June to August 1970) are believed due to calibration techniques, since calibration factors also changed. Data on experimental flares fired during the summer were examined to determine the effect of calibration changes. Work during this period was done largely to perfect mixing techniques and viscosity reproducibility, and optimization or binder development work was not affected.

Variations in the data on Mark 45 composition could not be attributed to variations in mixing, batch, or length of storage before firing. A group of these flares with 2-ply taped cases gave an average efficiency of 75,000 cd-sec/g. Therefore, the Dow "best efforts" composition with 70,000 cd-sec/g efficiency is expected to give about 5,000 cd-sec/g less luminous efficiency than the Mark 45 composition at approximately the same burning rate when fired in 1-1/4-inch diameter using 2-ply taped case material.

## SECTION VII

### OTHER BINDER SYSTEMS INVESTIGATED

#### A VINYL ESTER RESINS

A Dow experimental vinyl ester resin, based on HEA (hydroxyethyl acrylate) and MA (maleic anhydride) at a 54.2/45.8 ratio, diluted with 40 percent HEA, required 24 hours to cure at 100°C in the absence of catalyst. Free radical catalysis with cumene hydroperoxide or lauroyl peroxide accelerated the cure rate significantly and produced a more densely cross-linked gumstock. This relatively high oxygen (40 percent) binder, formulated as a complete flare mix, gave a luminous efficiency at 24 percent binder of only 9,000 cd-sec/g. Attempts to increase light output by adding TEGDN resulted in extreme gassing and poor curability. Incorporation of D.E.R.<sup>®</sup> 736 and increasing the catalyst concentration noticeably reduced grain expansion and improved curing rate.

Presumably, preferential reactivity of glycidyl ether with carboxylic groups contributes to overcoming magnesium incompatibility, resulting in reduced gasification and grain expansion.

#### B ALLYL DIGLYCOL CARBONATE

It was found possible to increase the oxygen content of the low viscosity monomer allyl diglycol carbonate (ADGC) by free radical copolymerization with MA. A 100.0-gram flare mix was prepared with 19 percent binder containing a ratio of 3 moles of ADGC to 2 moles of MA, catalyzed with 1.0 percent lauroyl peroxide. Castability was threshold, the cured grain was firm but low in cohesive strength, and grain expansion was totally absent. A single candle was fired and yielded a luminous efficiency slightly in excess of 50,000 cd-sec/g at a burning rate of 0.061 in/sec. This is an unusually high efficiency for a composition with no nitro-plasticizer.

An interesting gumstock was prepared by copolymerizing ADGC with the HEA-diluted vinyl ester of HEA and MA. It was characterized by low viscosity and very high thermal stability. The oxygen content of this binder (45 percent) qualifies it for future consideration.

#### C TRIS(HYDROXYMETHYL)NITROMETHANE

As seen in Table XI, several nitro-containing compounds and oxygen-rich acids were investigated as eutectic curing agents in combination with ethylene carbonate. Because of

TABLE XI. EC EUTECTICS

Compound	Eutectic Range	Reactivity
Nitrilotriacetic acid (NTA)	None	--
Dinitrosalicylic acid (DNSA)	25-40%	Violent with XFS-4008L and Mg
Dinitroaniline (DNA)	None	--
Dinitrophenol (DNP)	15-25%	Violent with Mg
Oxalic acid	None	--
Citric acid	None	--
Maleic acid	None	--
Pyromellitic acid (PMA)	None	--
Pyromellitic dianhydride (PMDA)	None	--
Tris-nitro	18-35%	No immediate reactivity with Mg, NaNO <sub>3</sub> , or XFS-4008L

composition compatibility, only the tris(hydroxymethyl) nitromethane (tris-nitro) eutectic (53 percent oxygen) appears sufficiently promising for additional studies.

Initial qualitative studies revealed a potentially interesting high oxygen binder composed of tris-nitro and MA. The uncatalyzed curing rate was very slow, but future effort is warranted.

#### D NON-PLASTICIZED SYSTEMS

The major drawback of nitro-plasticizers is the tendency to migrate or exude, especially when present in large amounts. Some effort was directed at developing castable, non-plasticized compositions that might produce high light output.

##### 1 XFS-4008L - Ethylene Glycol - Triethanolamine

Epoxy-hydroxyl reactions can be promoted by inorganic bases and tertiary amines. Initial investigation of neat binders revealed that glycerine and ethylene glycol cure XFS-4008L in the presence of BDMA (benzyl dimethylamine) or aqueous NaOH. The glycerine-based binder produced very high viscosity; however, ethylene glycol showed a more promising castability. An interesting feature of ethylene glycol, in addition to the low viscosity and high oxygen content (52 percent), is its solubilizing effect on  $\text{NaNO}_3$  (approximately 15 percent). This is important for castability at lower binder levels.

It was also found that tertiary hydroxyl-containing TEA (triethanolamine) is a better solvent for  $\text{NaNO}_3$  than BDMA. A curable ratio of 77.4 percent XFS-4008L, 17.1 percent ethylene glycol, and 5.5 percent TEA was first studied, but to obtain improved castability, a ratio of 59.1 percent XFS-4008L, 30.4 percent ethylene glycol and 10.5 percent TEA was employed. Utilizing this ratio, fully formulated flare composition was mixed, containing:

34.5% magnesium, 40/200  
48.5%  $\text{NaNO}_3$ , <400 mesh  
17.0% binder.

The mix proved to be semi-castable at room temperature, cured hard within 1/2 hour at 108°C, and produced a luminous efficiency of 30,000 cd-sec/g at a burning rate of 0.030 in/sec. When the metal to oxidizer ratio was raised, this system achieved an efficiency of 58,400 cd-sec/g, at a burning rate of 0.032 in/sec. This semi-castable composition contained:

44.5% magnesium, 40/200  
37.5%  $\text{NaNO}_3$ , <400 mesh  
18.0% binder.

Although these data represent an initial investigation on a single candle, this binder system remains encouraging.

Substitution of the low viscosity epoxy resin D.E.R.<sup>®</sup> 736 for XFS-4008L in this system appears promising from a castability standpoint, but nitrate plasticization probably will be necessary for high luminous efficiency.

## 2 Solubility of Sodium Nitrate

Since high concentrations of small particle size, irregularly shaped, crystalline  $\text{NaNO}_3$  required for efficient combustion and proper burning rate are detrimental to castability, particularly in non-plasticized compositions, a limited effort was directed at solubilizing  $\text{NaNO}_3$ .

Above 42°C, a 1 to 1 ratio of  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , produced a very fluid dispersion. When mixed with the remaining flare composition ingredients, this produced a highly fluid, non-plasticized composition. However, grain expansion and gassing in the presence of magnesium rendered this approach impractical.

Formamide, a possible low viscosity reactive curing agent or diluent, shows a relatively high solubilizing ability for  $\text{NaNO}_3$  but inhibits curing of XFS-4008L.

## E MORE ENERGETIC PLASTIZIERS

Several attempts to utilize nitroglycerine (NG) failed to produce firm, hard, non-porous candles. This may be due to the presence of unremoved traces of desensitizing solvent. Preliminary sensitivity data on a flare composition containing:

49.0% Mg, 40/200  
27.0%  $\text{NaNO}_3$ , <400 mesh  
16.3% XFS-4008L  
0.5% D.E.H.<sup>®</sup> 24  
7.2% NG (30% of binder)

exhibited a safe impact sensitivity,  $E_{50} > 200 \text{ Kg cm}$ . Although a non-propagating flash level was obtained at 0.0625 joule on the spark tester, flame propagation could not be achieved at the maximum instrument output of 18.75 joules. Because hazard testing indicated safe properties in a complete composition, an attempt was made to obtain a new supply of NG. Initial contact with a producer of NG, for the preparation of an XFS-4008L - NG solution, was well received.

An attempt at substituting diethyl oxalate (44 percent oxygen) for TEGDN or DEGDN proved encouraging, yielding equivalent light output and burning rate in initial tests. A composition containing 24 percent of XFS-4008L - MA - diethyl oxalate (54 percent) binder yielded 57,700 cd-sec/g efficiency and 0.055 in/sec burning rate, although the mix was not quite castable.

## SECTION VIII

### PARTICLE SIZE DISTRIBUTION OF MAGNESIUM AND SODIUM NITRATE

Because fuel and oxidizer particle size distributions are important for control of castability and combustion, it is desirable to utilize a constant source and type of each ingredient. Table XII shows the variation in particle distribution of 40/200 magnesium used at the beginning and end of this program.

TABLE XII. PARTICLE SIZE DISTRIBUTION OF  
ATOMIZED 40/200 MAGNESIUM

Sieve Size % on	Initial Lot Used	Final Lot Used
60	17.8	23.1
80	49.4	67.2
100	28.8	8.9
120	--	--
140	3.6	0.7
Pan	0.4	0.1

Surprisingly, these lots of atomized magnesium show a very low concentration of particles finer than 100 mesh and would be more aptly described by a 50/100 designation.

Figure 9 shows the size and structure of the atomized 40/200 magnesium magnified 45.6X. While there are some irregular particles, the material is mainly spherical. Many of the spheres have tiny particles on their surface. The possible rheological effect, however, should be very small. The multisized, rough surfaced  $\text{NaNO}_3$  crystals are shown in Figure 10. Particles of  $\text{NaNO}_3$  range from approximately 1 micron to 80 microns, where greater than 50 percent by weight are larger than 25 microns, only about 1.0 percent are less than 5 microns, and only about 1.0 percent are larger than 50 microns.



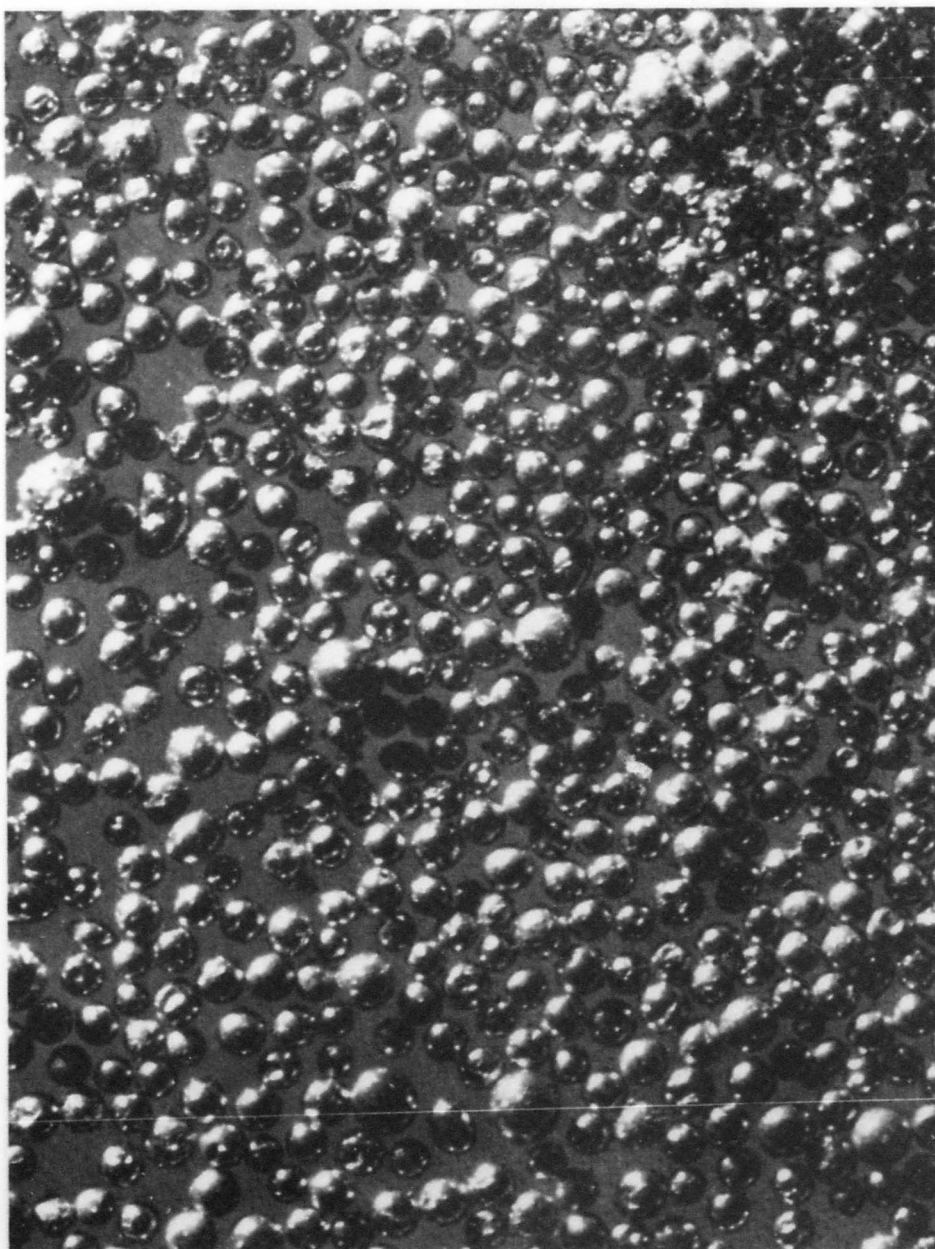


Figure 9. Photomicrograph of 40/200 Magnesium - 45.6X



Figure 10. Photomicrograph of Sodium Nitrate - 350X

## SECTION IX

### CONCLUSIONS AND RECOMMENDATIONS

Several promising flow-castable compositions have been developed during this program. The most efficient yield 60,000 to 70,000 cd-sec/g in 1.25-inch diameter candles, about 5,000 cd-sec/g less than MK 45 composition in the same configuration. It appears that 10 to 20 percent efficiency improvement is likely, if composition variables such as fuel/oxidizer ratio and binder level are altered. Therefore, it is recommended that further work be done on flow-cast flare compositions.

The most promising compositions are based on XFS-4008L epoxy resin, cured with and plasticized with the following:

- (1) EC-MA, DEGDN
- (2) EC-MA, TEGDN
- (3) MA, DEGDN
- (4) MA, TEGDN
- (5) XF-4012, DEGDN
- (6) XF-4012, TEGDN
- (7) D.E.H.<sup>®</sup> 24, DEGDN
- (8) D.E.H.<sup>®</sup> 24, TEGDN

System (1) has been studied fairly well, although further work is needed, particularly using larger diameter flares. Initial optimization work has been done at one Mg/NaNO<sub>3</sub> ratio for systems (4) and (5), but considerably more effort is desirable. Systems (2), (3), and (6) will be easier to optimize when data are available on the systems with the complementary plasticizer. Although no optimizing has been done on systems (7) and (8), these should be studied, since they are the most stable in surveillance.

Most of the work done has involved 1.25-inch-diameter flares. The effect on performance of using 3 to 4-inch candles should be studied. The effect of diameter on the composition optimum should also be determined.

To develop a practical flare composition, a satisfactory case material should be discovered. Using 3 to 4-inch-diameter candles, paper phenolic, cotton phenolic, cardboard, or aluminum tubes should be tested. It will probably be necessary to use a case bonding material. The unplasticized binders (where feasible) should be tested as well as Viton A and similar materials.

Experiments also should be undertaken to relate the laboratory process and materials used to prepare flare candles

to practical manufacturing processes. Various methods of preparing oxidizer should be investigated, with emphasis on eliminating the 400 mesh screening step. Mixing tests should be conducted using equipment generally available in propellant and pyrotechnic processing facilities. Allowable limits on magnesium type, particle size, and size distribution should be determined.

XFS-4008L is a satisfactory high oxygen binder resin, and binders based on it contain 40 to 50 percent oxygen. It should be possible to obtain binders with higher oxygen levels by preparing resins with greater oxygen content or by using higher oxygen plasticizers. Binders containing nitro, nitrate, carbonate, or oxalate groups should be of special interest.

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13. ABSTRACT Research and development studies have been conducted on flow-castable magnesium - sodium nitrate flares. The epoxy resins XFS-4008L (glycerin diglycidyl ether) and diglycidyl carbonate were evaluated. The curing agents XF-4012 (partial nitrate salt of amine-terminated polypropylene glycol), maleic anhydride (MA), maleic anhydride - ethylene carbonate (EC), maleic half esters, glycol, benzyldimethylamine and D.E.H. <sup>®</sup> 24 (triethylenetetramine) were investigated. TEGDN (triethyleneglycol dinitrate), DEGDN (diethyleneglycol dinitrate), and BDNPA/F [1-1-solution of bis-(2,2-dinitropropyl)acetal and bis(2,2-dinitropropyl) formal] were tested as plasticizers. The most favorable results were obtained with XFS-4008L resin; XF-4012, MA, EC-MA, or D.E.H. <sup>®</sup> 24 curing agent; and TEGDN or DEGDN plasticizer. Flare compositions containing these binders can be mixed, poured, and cured; display low spark or impact sensitivity; and are adequately stable in storage at 70°C for 4 to 12 weeks. A "best efforts" composition, containing 22 percent of XFS-4008L - EC-MA - DEGDN binder, yielded an efficiency of 70,000 cd-sec/g (candle-seconds per gram) at 0.056 in/sec (inch per second) burning rate in a 1.25-inch-diameter tape-wrapped flare.		

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